Correlation of Pure Component Gibbs Energy Using UNIFAC Group Contribution

The UNIFAC group contribution method has already proved highly valuable for predicting excess Gibbs energies of liquid mixtures and hence vapor-liquid equilibria. The solution of groups concept is extended to cover the total Gibbs energy of any system, pure or mixed, relative to a well-defined standard state. The result is a correlation which is capable of predicting simultaneously pure component vapor pressures and standard Gibbs energies of formation and mixture vapor-liquid equilibrium compositions. The results presented strongly support the approach and indicate that the method should be further developed.

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The UNIFAC group contribution method proposed by Fredenslund, Jones, and Prausnitz (1975) has provided the design engineer with a rational and reliable basis for predicting activity coefficients in nonelectrolyte liquid mixtures. The reliability of the method is demonstrated by a large number of predictions (Fredenslund et al., 1977*b*). At present, UNIFAC (Fredenslund et al., 1977*a*, *b*) represents more than 70% of the published vapor-liquid equilibrium data at normal pressures.

The UNIFAC method is based on the solution of groups concept. The groups are structural units such as $—CH_3$, $—COCH_3$, $—COCH_2—$, $—CH_2Cl$, and others, which, when added, form the parent molecules. The excess Gibbs energy of a liquid mixture G^E is then determined by the properties of the groups rather than those of the molecules. G^E is the sum of two contributions: the combinatorial contribution representing nonideality due to differences in molecular sizes and shapes (estimated from group sizes and surface areas), and the residual contribution representing nonideality due to energetic interactions among groups (calculated from group interaction parameters and surface areas).

In the following, the solution of groups concept is applied to pure components at moderate pressures. No assumptions other than those stated above are needed.

PURE COMPONENT VAPOR PRESSURES

A pure component i is constituted from $\nu_k^{(i)}$ groups of type k, $k = 1, 2 \ldots L$, where L is the number of different groups in component i. The total number of groups in molecule i, $\nu^{(i)}$, is given by

$$\nu^{(i)} = \sum^{k} \nu_k^{(i)} \quad k = 1, 2 \ldots\ldots L \tag{1}$$

and the fraction of group k in pure component i is

$$X_k^{(i)} = \nu_k^{(i)}/\nu^{(i)} \tag{2}$$

UNIFAC was previously applied to saturated liquid mixtures. By analogy, the Gibbs energy of pure component i at pressures not far from saturation is given by

$$G_i = \sum^{k} \nu_k^{(i)} g_k + \nu^{(i)} \Delta g_i^{id} + \nu^{(i)} g_i^E \tag{3}$$

where the first term is the sum of the pure group free energies, Δg_i^{id} is the ideal Gibbs energy of mixing of one mole of groups, and g_i^E is the excess Gibbs energy for one mole of groups. One mole of molecules i gives rise to $\nu^{(i)}$ moles of groups. The index i on Δg_i^{id} and g_i^E serves as a reminder that the properties are evaluated at the group composition $X_k^{(i)}$ corresponding to pure component i. It follows that

$$G_i = \sum^{k} \nu_k^{(i)} g_k + RT \sum^{k} \nu_k^{(i)} \ln X_k^{(i)} + \nu^{(i)} g_i^E \tag{4}$$

We need now to define the reference Gibbs energy of component i, and we choose the perfect gas at temperature T and 1 atm pressure. For the perfect gas at 1 atm, we assume

$$G_i^o = \sum^{k} \nu_k^{(i)} g_k^o + RT \sum^{k} \nu_k^{(i)} \ln X_k^{(i)} \tag{5}$$

Thus

$$G_i - G_i^o = \sum^{k} \nu_k^{(i)} (g_k - g_k^o) + \nu^{(i)} g_i^E \tag{6}$$

Using classical thermodynamics and defining $\Delta g_k = (g_k - g_k^o)$, we obtain

$$RT \ln f_i = \sum^{k} \nu_k^{(i)} \Delta g_k + \nu^{(i)} g_i^E \tag{7}$$

For convenience, we assume that the vapor phase fugacity coefficients are unity. [If not, they may be evaluated using Hayden and O'Connell's (1975) method for predicting second virial coefficients.] Neglecting the Poynting correction factor, one obtains

$$G_i - G_i^o = RT \ln P_i^{\text{sat}} = \sum^{k} \nu_k^{(i)} \Delta g_k + \nu^{(i)} g_i^E \tag{8}$$

Following UNIFAC, we assume that g_i^E is given in terms of the residual group activity coefficients $\Gamma_k^{(i)}$ evaluated at composition $X_k^{(i)}$; thus

$$G_i - G_i^o = RT \ln P_i^{sat} = \sum^{k} \nu_k^{(i)} \Delta g_k + RT \sum^{k} \nu_k^{(i)} \ln \Gamma_k^{(i)} \tag{9}$$

$\Gamma_k^{(i)}$ is calculated from van der Waals group surface areas and UNIFAC group interaction parameters. For this purpose, it is necessary to use the same group definitions as Fredenslund et al. (1977*b*).

One may argue that perhaps a combinatorial contribution should be included in $\nu^{(i)} g_i^E$. However, since the group sizes do not differ greatly, this term may be safely neglected here. A contribution due to the specific configuration of the groups when forming the molecules is not necessary here because this term is the same for both G_i and G_i^o and, hence, cancels.

When values of Δg_k are available for all groups, pure

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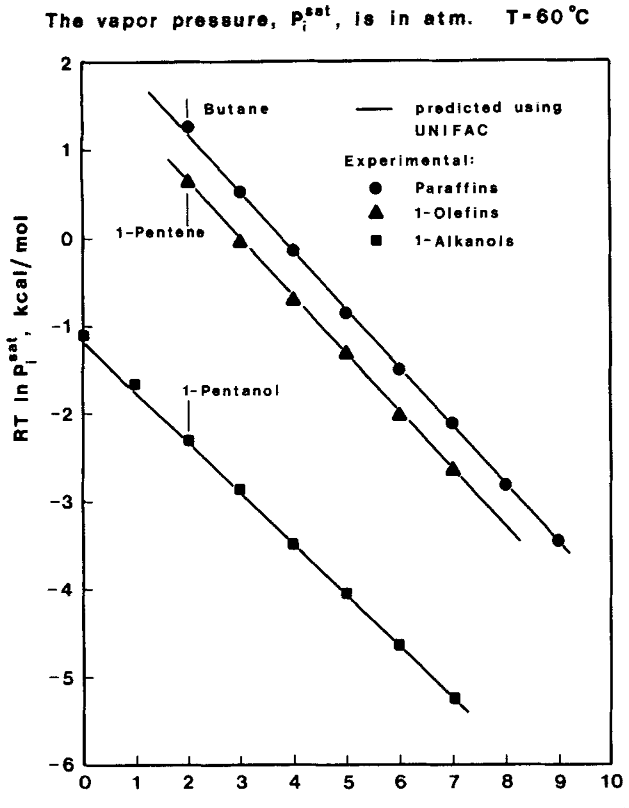

Fig. 1. Experimental and predicted vapor pressures for normal paraffins, 1-olefins, and 1-alkanols.

component vapor pressures may be predicted using the already established UNIFAC parameters. Or, conversely, group interaction parameters not otherwise available may be estimated from vapor pressures of pure substances.

The following values of Δg_k are estimated from pure component vapor pressures at 60°C:

$\Delta g_{CH_3} = 1.23$ kcal/mole $\quad \Delta g_{CH_2=CH} = 0.40$ kcal/mole

$\Delta g_{CH_2} = -0.66$ kcal/mole $\Delta g_{CH_2CH_2OH} = -2.78$ kcal/mole

The vapor pressures of various pure substances may now be calculated. Figure 1 shows predicted vapor pressures of homologous series as functions of the number of CH_2 groups in the molecules [for pentane, $\nu_{CH_2}^{(i)} = 3$, 1-propanol, 0; 1-butanol, 1; 1-pentene, 2; 1-hexene, 3; etc.]. Figure 1 shows excellent agreement between the predicted and experimental results. It should, however, be noted that

1. Δg_k is, unlike the UNIFAC group interaction parameters, dependent on temperature. The temperature dependence of Δg_k may be readily established (Reid et al., 1977).

2. $\nu^{(i)} g_i^E$ is often on the order of 10% of $\sum^{k} \nu_k^{(i)} \Delta g_k$, which renders the determination of UNIFAC parameters from pure component vapor pressures difficult (but not impossible).

3. Δg_k for CH_2 is, unlike the UNIFAC group interaction parameters, dependent upon whether the CH_2 group is in a straight chain alkane or in a cyclic alkane. (The value listed above is for straight chain alkanes.)

STANDARD GIBBS ENERGY OF FORMATION

In Equation (5), G_i^o may be interpreted as the standard Gibbs energy of formation of component i from the elements in their natural states at temperature T and a pressure of 1 atm. g_k^o may be similarly interpreted for group k.

When g_k^o is known, G_i^o may be calculated from Eq. (5).

The following values of g_k^o are estimated from values of G_i^o for straight chain compounds at 400°K given by Stull et al. (1969):

$g^o_{CH_3} = -0.88$ kcal/mole $\quad g^o_{CH_3CO} = -28.34$ kcal/mole

$g^o_{CH_2} = 4.68$ kcal/mole $\quad g^o_{CH_2CH_2OH} = -27.04$ kcal/mole

$g^o_{CH_2=CH} = 22.50$ kcal/mole

$g^o_{CH_3NH_2} = 18.00$ kcal/mole

Table 1. Comparison between Standard Gibbs Energies of Formation at 400°K from Literature (Stull et al., 1969) and Those Predicted Using Equation (5)

Substance i	G_i^o from literature, kcal/mole (A)	Predicted value of G_i^o, kcal/mole (B) equation (5)	Deviation, (A-B) kcal/mole
Butane	5.10	5.40	−0.30
Hexane	13.96	13.92	0.04
Octane	22.78	22.74	0.04
Decane	31.64	31.70	−0.06
1-pentene	27.37	27.67	−0.30
1-heptene	36.20	36.20	0.00
1-nonene	45.07	45.03	0.04
Acetone	−31.12	−30.32	−0.80
2-butanone	−27.15	−27.16	0.01
2-pentanone	−22.55	−23.17	0.62
1-butanol	−25.61	−25.86	0.25
1-hexanol	−17.73	−17.66	−0.07
1-octanol	−7.97	−8.95	0.98
1-decanol	−0.30	−0.05	−0.25
Ethylamine	15.92	16.02	−0.10
Propylamine	18.94	19.18	−0.26
Butylamine	23.61	23.17	0.44

In Table 1, values for G_i^o predicted using Equation (5) are compared with values listed by Stull et al. (1969). The results from Equation (5) appear to be as good as or better than the results from the method for predicting G_i^o by van Krevelen and Chermin (1951) [see Reid et al. (1977), pp. 278-285]. As before, g_k^o depends upon temperature and on whether the group is in a straight chain or in a cyclic compound.

CONCLUSION

It is possible within the group contribution approach and the UNIFAC method to correlate pure component properties. This note together with previous publications on UNIFAC for liquid mixtures amounts to a unified account for group contribution prediction of the Gibbs energy of pure liquids and of liquid mixtures. The result is a framework for simultaneously correlating vapor pressures and liquid phase activity coefficients using the same group interaction parameters, here UNIFAC. A model for predicting standard Gibbs energies of formation is contained within the framework. Whereas much attention has already been given to the application of UNIFAC to liquid mixtures, much work needs to be done before the method may be generally applied to pure components. We have shown that such an effort should have a reasonable chance of success.

NOTATION

f_i = fugacity of pure component i, atm
G_i = Gibbs energy of 1 mole of liquid component i, kcal/mole
G_i° = Gibbs energy of 1 mole of component i in its standard state, kcal/mole
G_m = Gibbs energy of 1 mole of liquid mixture, kcal/mole
G_m° = Gibbs energy of 1 mole of mixture in its standard state, kcal/mole
G^E = excess Gibbs energy of 1 mole of mixture, kcal/mole
g_k = Gibbs energy of 1 mole of group k, kcal/mole
g_k° = Gibbs energy of 1 mole of group k in its standard state, kcal/mole
g^E = excess Gibbs energy of 1 mole of groups, kcal/mole
g_i^E = excess Gibbs energy of 1 mole of groups at the composition corresponding to pure component i kcal/mole
P_i^{sat} = vapor pressure of component i, atm
R = gas constant, kcal/mole °K
T = temperature, °K
x_i = mole fraction of component i
X_k = group fraction of group k
$X_k^{(i)}$ = group fraction of group k in pure component i
Γ_k = residual activity coefficient of group k
$\Gamma_k^{(i)}$ = residual activity coefficient of group k at composition $X_k^{(i)}$
$\nu^{(i)}$ = total number of UNIFAC groups in component i
$\nu_k^{(i)}$ = number of UNIFAC groups of type k in component i

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BOOKS

Transport in Porous Catalysts, by R. Jackson, Chemical Engineering Monographs Vol. 4, Elsevier Scientific Publishing Co., New York, 1977. (197 pages, $29.80).

Very infrequently there appears a concise carefully written and comprehensible monograph with sufficient rigor that it soon becomes a standard reference and guideline for the student, the researcher and the practitioner. Professor Jackson has accomplished such a feat in this monograph which brings together material from the technical literature of the past hundred years or so and gives a connected account of transport in porous media relative to modeling catalyst pellets. It is ideally suited for a first graduate-level course in chemical reaction engineering. Furthermore, practicing engineers will find it refreshing to read and thoroughly informative.

Professor Jackson develops the theory of diffusive transport for ideal gas mixtures in porous catalysts in a general form rather than limiting the treatment to simple binary systems which so often have been used to approximate the real situation. In addition, he considers transport in pores having intermediate sizes wherein pore diameters and molecular mean free paths are comparable in magnitude. He aptly calls it the "awkward" range because the prediction of transport behavior for that situation, which frequently occurs in practice, is by no means trivial and often has been a source of confusion.

Professor Jackson is particularly helpful in exposing erroneous conclusions that one, quite unwittingly, may reach. He very skillfully keeps the reader informed about the physical meanings of the formulations which are developed.